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FELLOWSHIP FINAL REPORT

CosmOrbitrap - high resolution mass spectrometer for space application

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REPORT INFO

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ABSTRACT

A scientific request for an efficient instrument for unambiguous in-situ analysis of the composition of the Solar system rises up, since an abundance of complex organic compounds at planets, moons and interplanetary medium has been experimentally confirmed. New experimental data will unveil chemical history of the Solar System and probable mechanisms of formation of extraterrestrial organic compounds. A space-grade Orbitrap™-based high-resolution mass spectrometer will allow to obtain required data. In scope of this research project, Lab-CosmOrbitrap and OLYMPIA mass analyzer instruments developed within the CosmOrbitrap project were optimized. New sampling systems and ionization mechanisms proposed for the future space-grade instruments have been developed and evaluated. Experimental calibration data for solid (the real Moon fragment) and gaseous samples (He, C_2H_4, N_2 and CO) required for the currently designed space instruments (CRATER, CORALS and HANKA) were measured.

1- Introduction

In situ measurements during last space missions to Saturn and its moons (Cassini-Huygens (Waite *et al.*, 2005; Woodson *et al.*, 2015)) and the 67P/Churyumov-Gerasimenko comet (Rosetta (Kissel *et al.*, 2007; Taylor *et al.*, 2017; Grady *et al.*, 2018)) have provided data on the composition of the Solar System's bodies and interplanetary environment. Its complex organic and mineral composition has been confirmed. However, performance of flight-ready instruments currently available for the *in-situ* analysis of the chemical composition is not sufficient for unambiguous identification of complex molecules in the component rich mixtures.

Scientific group of Dr. Christelle Briois (LPC2E, Orléans), as a part of CosmOrbitrap consortium of 6 laboratories, works on development of the space instrument capable to such *in situ* analysis of extraterrestrial objects. The CosmOrbitrap is a project aimed to create a spaceflight adapted version of the commercial Orbitrap™ (Thermo Fisher Scientific) mass analyzer (Briois *et al.*, 2016). This technology is highly demanded for approved by NASA and ESA currently designed CORALS,CRATER and HANKA space instruments aiming to analyze the composition of (sub)surface of the Europa and the Moon. Orbitrap™ is a mature industry standard technology of high-resolution mass spectrometry (Makarov, 2000; Eliuk and Makarov, 2015). The task of this study was to analyze trade-offs of the miniaturization and simplification of the commercial Orbitrap™ instrument design and to determine its optimal configuration for work with different ion sources.

2- Experimental details

There are two different High-Resolution Mass Analyzers (HRMS) operated at the LPC2E laboratory under the CosmOrbitrap project: LAb-CosmOrbitrap – a high TRL (space flight readiness) level prototype of the space-based mass spectrometer and Orbitrap anaLYseur MultiPle IonisAtion (OLYMPIA) - a laboratory mass spectrometer and technology test workbench device. The latter instrument has been developed in a collaboration with J. Heyrovsky institute of physical chemistry (Czech Republic).

One of the main tasks related to this setup is to build a HRMS device capable of operation with different ion sources. This fact allows to perform laboratory studies of samples in different states (gaseous, liquid or solid) and test no C-trap configuration of the Orbitrap-based instrument (Makarov *et al.*, 2006) with different ion sources. The first phase of this research project was development of a numerical model of the ion source and optics using a SIMION software package (the field and particle trajectory simulator) and verification of optimal parameters for the ionization and ion beam transport. This simulation data have been used to find an optimal ionization method and configuration of the ion optics.

OLYMPIA setup

This is a new instrument (figure 1), tested with electron ionization (EI) source and prepared to work with the Laser Induced Liquid Bead Ion Desorption (LILBID) setup. Design of the new ion optics required to transport ions from the source to the Orbitrap™ cell has been verified both experimentally and using a developed numerical model (figure 2). The distribution of the kinetic energy of ions (figure 3), timing and divergence of the beam, which is important for trapping of ions, have been studied. This confirms the possibility to operate EI source in the continuous mode, and thus simplify high voltage electronic system.

Figure 1. OLYMPIA setup

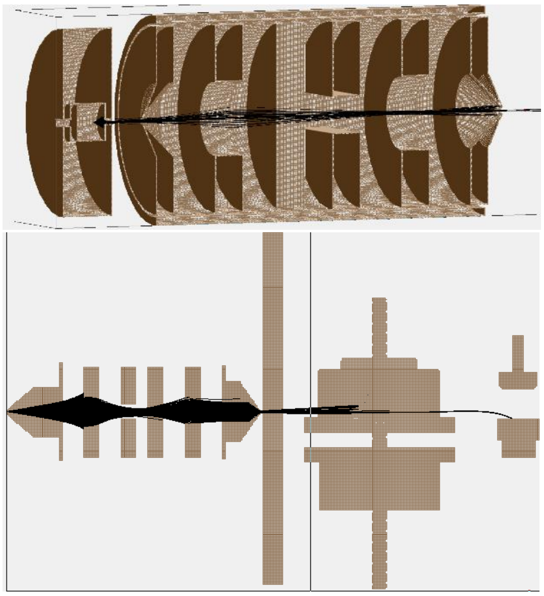


Figure 2. Numerical model of the ion beam transport developed using SIMION software package: extraction of ions from the source (upper panel) and ion beam transport (bottom panel).

Different data acquisition (e.g. custom made two stage pre-amplifier) and processing systems have been tested. These tests provided experimental data necessary to differentiate processing induced and instrument configuration specific signal distortions. The computational complexity effective FFTW algorithm (Frigo and Johnson, 1998) have been implemented. This allows to diminish sample processing time (for the 16 bit, 20MHz, 20 – 1000 ms digitized signal) making it comparable to its acquisition duration using a commercially available laptop. High efficiency of the processing software is expected to be useful for the analysis of large amount of experimental data acquired during the future space missions.

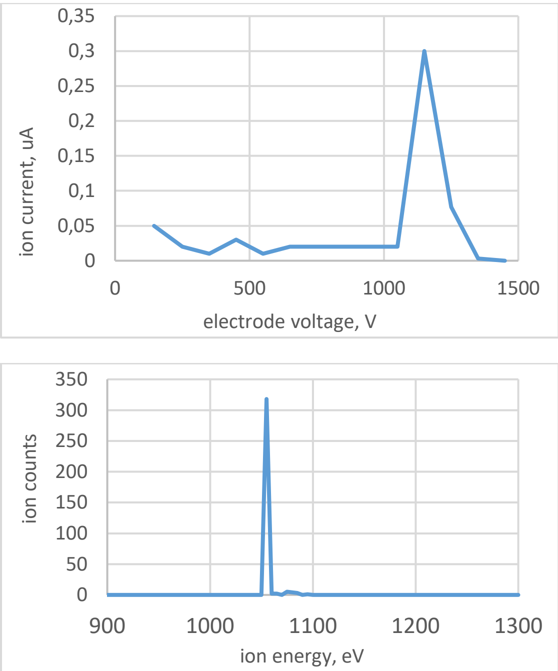


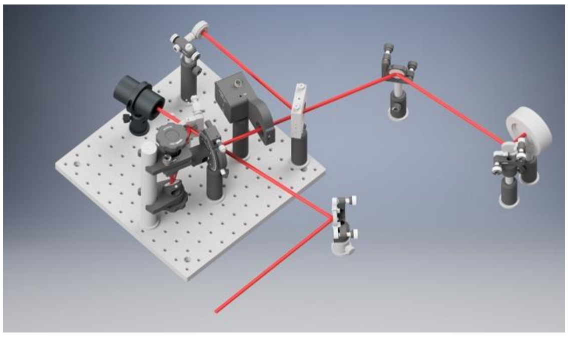
Figure 3. Experimentally measured (upper panel) and calculated (bottom panel) kinetic energy distribution of ions after the ion optics.

LAb-CosmOrbitrap setup

The operation principles and design of the LAb-CosmOrbitrap HRMS instrument are described in Briois *et al.*, 2016 and Selliez *et al.*, 2019. Mass resolution of the instrument varies from 474,000 to 90,000 for a 9 to 208 m/z range (Briois *et al.*, 2016) and is sufficient to resolve complex organic compounds in its mixtures (Selliez *et al.*, 2018, 2019).

According to the numerical study using the SIMION model, the mass spectrometry analysis of different areas of the studied sample can be performed by laser scanning over the sample surface without changing of the sample position. The laser focal spot position can be changed, and in this way different part of the sample can be ionized. After ionization, ions can be extracted from the ion source, injected into to the Orbitrap™ using the ion optics system and analyzed. An offset of the focal spot for less that 5 mm away from the center of sample holder makes no significant impact on the signal intensity.

Respectively, a new steering mirror system for laser focal spot positioning and scanning has been designed, constructed and tested (figure 4). Also, laser optics has been modified to work with 213 nm laser beam, which has been used to study geological samples that contain optically transparent fragments (e.g. Moon's regolith). This optical system allows to enrich the laser spectrum for 213 nm component by mounting the 5ω high-harmonic generation module, to manipulate the laser focal spot position and adjust the pulse energy in the range of 0 – 150 μJ.



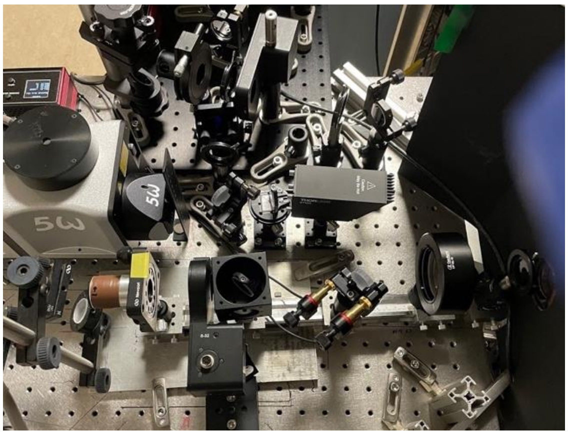


Figure 4. Design (upper panel) of the 213 nm laser with adjustable energy pulse and focal spot position, and implementation (bottom panel) of the switchable 266 nm and 213 nm laser optical system.

3- Results and discussion

Measurement of the composition of gas samples using the EI source

Resulting mass resolution of the OLYMPIA HRMS instrument is sufficient to resolve different components with the same molecular mass in the $C_2H_2/CO/N_2$ mixture (figure 5). For this mass range, mass resolution of $m/\Delta m \approx$ 40 000 has been achieved . However, the use of signal acquisition time longer than 250 ms reduces an accuracy of the component fraction ratio. This ratio is also affected by the ionization efficiency of specific molecules and further chemical reactions in the ion source. Thus, prior laboratory calibration measurements are necessary for *in situ* composition analysis of gaseous extraterrestrial samples (e.g. dense atmospheres of planets).

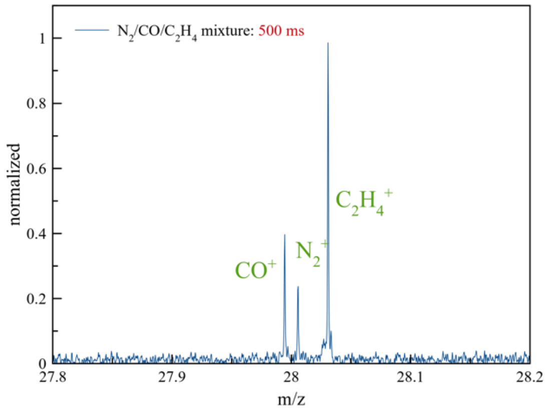


Figure 6. Experimental mass spectra of the $C_2H_2/CO/N_2$ mixture at *m/z* 28 measured with 500 ms acquisition time.

Concept proof study of real Moon fragment study using the 213 nm enriched laser ablation ion source

Experimental spectra of basal geological standard and real Moon meteorite fragment have been measured with LAb-CosmOrbitrap to verify feasibility of the use of 213 nm wavelength laser for the laboratory analysis of mineral samples. An unambitious identification of metal atoms allows to compare the composition of space-relevant soils with calibrated laboratory standards (e.g. BCR-2 standard collected from Columbia River), so its structure can be identified. Higher photon energy (≈ 6 eV) is closer to the ionization energy of atoms and molecules. A range of chemical elements (e.g. Na, Al, Ti, V…) can be ionized in the single photon regime (lower laser pulse energy), so no destructive plasma conditions are required.

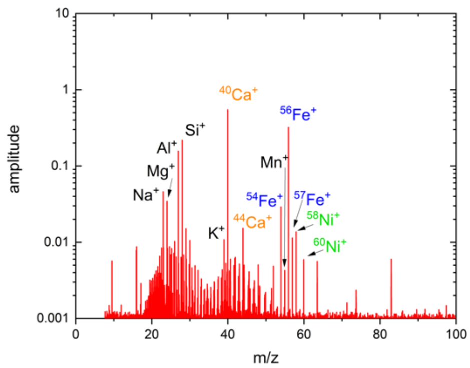


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Figure 7. Mass spectrum of the Moon meteorite fragment

4- Conclusions

Provided verification of the compatibility of the Orbitrap™ based HRMS instrument with different ion sources and the sampling spot scanning concept for solid surface analysis are important for design of the future space missions, such as the Moon lander or low Earth orbit cosmic dust analyzer.

The configuration of the Orbitrap™ based HRMS without the C-trap module is efficient up to the resolution of 30 000 – 50 000 over the mass range of *m/z* 28 – 86 mass units also for the continuous EI ion source that was used for the gas-phase samples. Nevertheless, such simplification of the instrument design may result in a certain underdensity of the gas composition measurement, especially for less abundant components of mixtures.

5- Perspectives of future collaborations with the host laboratory

Experimental data and technical experience obtained during this project have created a strong basis for the collaboration between Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), J. Heyrovsky Institute of Physical Chemistry, ELI Beamlines - International Laser Research Centre and Institut für Geologische Wissenschaften, Freie Universität Berlin to design CRATER (a laser CosmOrbitrap based instrument for a Moon lander) and SLAVIA (low Earth orbit spacecraft space missions-, as to develop a concept of a prospective space mission to Saturn, Jupiter and it's moons (CORALS, another laser CosmOrbitrap based instrument).

6- Articles published in the framework of the fellowship

At least one scientific paper based on the experimental results of this project is expected to be published and is currently undergoing the final stage of its preparation.

Results of this work have been presented at scientific conferences with published conference proceedings:

- Zymak, I., Sanderink, A., Gaubicher, B., Žabka, J., Lebreton, J.-P., Briois, C., 2021. OLYMPIA - a compact laboratory Orbitrap-based high-resolution mass spectrometer laboratory set-up: Performance studies for gas composition measurement in analogues of planetary environments, in: EGU General Assembly Conference Abstracts. AA(Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), UMR7328 CNRS/Université d'Orléans/CNES, 3A, Avenue de la Recherche Scientifique, 45071 Orléans, France), AB(Laboratoire de Physique et Chimie de l'Environnement et de l'Espace, pp. EGU21-8424.
- Arnaud Sanderink, Fabian Klenner, Illia Zymak, Jan Zabka, Frank Postberg, Christelle Briois, Bertrand Gaubicher, Bernd Abel, Ales Charvat, Jean-Pierre Lebreton, Barnabé Cherville and Laurent Thirkell, OLYMPIA-LILBID: A new Approach for Calibrating Spaceborne Hypervelocity Ice Grain Detectors Using High-Resolution Mass Spectrometry: American Geophysical Union, Fall Meeting; 2021:P15A-09

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